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## (54) MANUFACTURE OF HIGHLY CORROSION-RESISTANT RARE-EARTH MAGNET

(57)Abstract:

PURPOSE: To provide a method for manufacturing a highly corrosion-resistant rare-earth magnet which can maintain improved magnetic characteristics over a long period of time without generating hydrogen occlusion, etc.

-CONSTITUTION: RE-B-Fe sintered rare-earth magnet or RE-TM-B hot machining rare-earth magnet is heated at 200-500°C under oxidation atmosphere (a) or is anodized within an alkali liquid solution.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The manufacture approach of the high corrosion resistance rare earth magnet characterized by heating a RE-B-Fe system sintering rare earth magnet or a RE-TM-B system hot-working rare earth magnet (RE expressing one or more sorts of rare earth elements, and TM expressing one or more sorts of a transition element, respectively) at 200-500 degrees C under an oxidizing atmosphere.

[Claim 2] The manufacture approach of the high corrosion resistance rare earth magnet characterized by carrying out anode plate electrolysis of a RE-B-Fe system sintering rare earth magnet or the RE-TM-B system hot-working rare earth magnet (RE expressing one or more sorts of rare earth elements, and TM expressing one or more sorts of a transition element, respectively) in an alkaline solution.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Industrial Application]** This invention relates to the approach of having enabled it to maintain the magnetic properties which raised corrosion resistance and were excellent for a long period of time to manufacture a high corrosion resistance rare earth magnet.

**[0002]**

**[Description of the Prior Art]** Although the magnet alloy is broadly used from the peripheral device of a mainframe computer as the electrical and electric equipment or the charges of electronic-parts material for home use, such as various electric products, military requirements to a magnet alloy, such as magnetic properties and corrosion resistance, are advanced increasingly with the demand of the miniaturization of the computer especially in recent years, or an electric product, and high-performance-izing.

**[0003]** It is expected that it is meanwhile and a RE-B-Fe system sintering rare earth magnet and a RE-TM-B system hot-working rare earth magnet (it is the same below : to which RE expresses one or more sorts of rare earth elements, and TM expresses one or more sorts of a transition element, respectively) are excellent in magnetic properties. However, this rare earth magnet has the fault of it not only containing rare earth elements with very high activity, but the effect of the local battery by the potential difference between bi-phases also being added, and being very easy to rust since it is the alloy with which RE rich phase and Fe rich phase are intermingled. Therefore, the method of performing chemical conversion, such as approach; phosphating to which the surface treatment for rust proofing is indispensable to, for example, galvanizes metals and those alloys, such as nickel and Zn, in utilization, and chromate treatment; the method of performing resin coatings, such as epoxy system resin and acrylic resin, with dip coating, a spray method, etc. is proposed. nickel alloy-plating methods, such as nickel plating which can be carried out comparatively cheaply, or nickel-P, are used widely also especially in these, without requiring a complicated facility.

**[0004]**

**[Problem(s) to be Solved by the Invention]** However, by the approach of galvanizing a metal or alloys, such as nickel, satisfying plating adhesion and corrosion resistance are not necessarily acquired. One can be considered as follows [ the reason ]. That is, these rare earth magnets have high hydrogen absorption nature, and are considered with occlusion of the hydrogen generated in a rare earth magnet at the time of plating being carried out, causing a lifting and plating exfoliation for an embrittlement crack by the plating interface, and it becoming impossible to maintain corrosion resistance, when nickel or nickel alloy-plating method is adopted, since there is a property which stiffens by hydrogen absorption.

**[0005]** Although vapor-plating methods, such as vacuum evaporation plating, are also proposed in order to avoid such a problem, by this approach, the pinhole defect of a plating layer serves as a serious failure of corrosion-resistant improvement. Moreover, with dip coating, a spray method, etc., adhesion and corrosion resistance sufficient also by the approach of performing resin coating are hard to be acquired, it is difficult to form a uniform resin coating coat in a magnet front face moreover, and especially the magnetic edge section tends to become insufficient [ corrosion resistance ], and corrosion advances with this part as the starting point. This invention is made paying attention to the above situations, and the purpose tends to offer the approach for manufacturing the high corrosion resistance rare earth magnet which continues at a long period of time and can maintain outstanding magnetic properties, without producing problems, such as hydrogen absorption.

**[0006]**

**[Means for Solving the Problem]** The configuration of this invention which was able to solve the above-mentioned technical problem has a summary at the point which heats a RE-B-Fe system sintering rare earth magnet or a RE-TM-B system hot-working rare earth magnet at 200-500 degrees C under the (a) oxidizing atmosphere, or is anodized in (b) alkali solution.

**[0007]**

**[Function]** Although not all were solved about the reason whose corrosion resistance of a rare earth magnet improves by this invention, it is thought that it is because intermingled multiple oxides, such as an oxide of RE and Fe which are not formed under the usual atmospheric-air ambient atmosphere, or RE and TM, a hydroxide, and a hydrate, were probably firmly formed in the front face of \*\*, a RE-B-Fe system sintering rare earth magnet, or RE-TM-B system hot-working \*\*\*\*\*. In addition, although component ratios do not differ and the presentation of this oxide does not become fixed according to the conditions at the time of each alloy presentation or oxide film formation, since a rare earth magnet front face oxidizes, the problem of exfoliation is not produced. Furthermore, the above-mentioned multiple oxide has the very low solubility to water, and since it excels also in the stability over an elevated temperature, it is thought that degradation of the magnetic properties in years of use can be controlled.

**[0008]** The oxidizing atmosphere at the time of heating under an oxidizing atmosphere is not especially limited like steam Shimo under atmospheric air and oxygen tension adjustment that what is necessary is just to be under the environment which promotes oxidation. However, processing temperature cannot form the above-mentioned multiple oxide firmly, if it is good to consider as 200-500 degrees C and it is less than 200 degrees C, but since not only the oxidization on the front face of a magnet but oxidization of RE rich layer which deposits in the grain boundary will advance if it is 500 degrees C or more, it has a possibility that a crack may occur.

**[0009]** as the alkali solution at the time of anodizing -- alkali-metal hydroxides, such as KOH and NaOH, and Na<sub>2</sub> SiO<sub>3</sub> and KAlO<sub>2</sub> etc. -- a fusibility salt can also be added in this water solution that what is necessary is just one sort or two sorts or more of water solutions, such as an alkali-metal oxygen acid salt. Moreover, although pH of this water solution should just be alkalinity, it is desirable that it is the high alkalinity from which the dissolution of the magnet concerning this invention hardly takes place and which is like, and it is good that they are specifically ten or more pH. Furthermore, although what is necessary is just to determine suitably anode plate electrolytic conditions, such as solution temperature, current density, and dissolution time amount, according to a solution presentation or an alloy presentation, especially current density is 450 A/dm<sup>2</sup>. It is desirable that it is the following and it is considered that destruction of the formed multiple oxide is promoted more than by this. In addition, after performing each above-mentioned



processing, of course, it is also possible by preparing the chemical conversion and oxidation treatment of chromate treatment etc., an organic coating layer, etc. further to raise corrosion resistance further.

[0010] Next, the RE-B-Fe system sintering rare earth magnet and RE-TM-B system hot-working rare earth magnet which are used by this invention are explained. As rare earth elements indicated to be at least one sort of rare earth elements by RE including B and Fe as an essential element, first a RE-B-Fe system sintering rare earth magnet Pr, Nd, La, Ce, Tb, Dy, Ho, Er, Eu, Sm, Gd, Pm, Tm, Yb, Lu, Y, etc. can be mentioned, and these may be used independently, or two or more sorts can also be used together as occasion demands. Especially desirable things are Pr and Nd also in the above-mentioned rare earth elements.

[0011] The desirable content (hereafter, unless it mentions specially, atomic % is meant) of RE occupied in these RE-B-Fe system sintering rare earth magnet is 8 - 30%, coercive force sufficient at less than 8% is hard to be acquired, and if it exceeds 30%, a residual magnetic flux density will serve as insufficient feeling. Moreover, it is 2 - 28%, coercive force sufficient at less than 2% is hard to be acquired, and the desirable content of B will become inadequate [ a residual magnetic flux density ], if it exceeds 28% on the other hand. 40 - 90% of range of Fe is desirable, and at less than 40%, if a residual magnetic flux density serves as insufficient feeling and exceeds 90% on the other hand, the coercive force of a high level will become is hard to be acquired.

[0012] In addition, in the above-mentioned RE-B-Fe system sintering rare earth magnet, Co and nickel can also permute a part of Fe. However, since there is an inclination for a residual magnetic flux density to fall when the amount of permutations to Fe should be stopped to 50% or less and the amount of nickel permutations increases too much, since high coercive force will become is hard to be acquired if the amount of permutations of Co increases too much, the amount of permutations to Fe should be made 8% or less. Furthermore, it is possible by making Fe permute and contain one or more sorts of an element as shown in this magnet below as other elements to heighten coercive force further. However, although the permission content in the case of using two or more sorts together shows maximum among each alloying element, it makes a content an upper limit.

[0013] aluminum: Less than [ 9.5% ] Less than [ Ti:4.5% ] V:9.5% or less, Cr: Less than [ 8.5% ] Less than [ Mn:8.0% ] Less than [ Bi:5.0% ], Nb: Less than [ 9.5% ] Less than [ Ta:9.5% ] Less than [ Mo:9.5% ], W: 9.5% or less Less than [ Sb:2.5% ] Less than [ germanium:7.0% ], less than [ Sn:3.5% ] Less than [ Zr:5.5% ] Less than [ nickel:9.0% ], less than [ Si:9.0% ] Less than [ Zn:1.1% ] Less than [ Hf:5.5% ].

[0014] Next, although what was mentioned as RE as a configuration element of said RE-B-Fe system sintering rare earth magnet is again illustrated including at least one sort and transition element (TM) of rare earth elements (RE), and B containing Y as an essential element, a RE-TM-B system hot-working rare earth magnet Since the among these highest magnetic property is easy to be acquired when Pr is used, that [ Pr's ] whose 50% or more of RE is Pr is substantially desirable. Moreover, it is effective in improvement in coercive force to carry out little concomitant use of the heavy-rare-earth elements, such as Dy and Tb.

[0015] The desirable content of RE occupied in this RE-TM-B system hot-working rare earth magnet whole quantity is 12 - 18% of range still more preferably 10 to 20% more preferably 8 to 25%. Although the main phase of the magnet which makes RE, and TM and B a fundamental component is RE<sub>2</sub> TM<sub>14</sub>B (for example, Pr<sub>2</sub> Fe<sub>14</sub>B), since this compound will not be formed but it will become the cubic organization of the same structure as alpha iron if RE runs short, a good magnetic property (especially \*\*\*\*\*) is hard to be acquired, when there are too much another side and RE, nonmagnetic RE rich phase increases and a residual magnetic flux density comes to show a fall inclination.

[0016] Next, the content of B is more preferably [ 4 - 6% of ] suitable 2 to 8%. Since it becomes the rhombohedron of a RE-Fe system, when many [ the amounts of B run short and / that satisfactory coercive force is hard to be acquired / conversely / too ], it is nonmagnetic RE<sub>2</sub> Fe<sub>4</sub>. A B phase deposits and a residual magnetic flux density becomes low.

[0017] If TM is more preferably [ 65 - 90% of ] suitable and runs short of the amounts of TMs 40 to 90%, a residual magnetic flux density becomes low, and if many [ too ], it will become inadequate [ coercive force ]. In addition, although the most typical thing is Fe among TMs, Co and/or nickel can be substituted for the part. Although Fe site of the main phase is permuted that Co is effective in getting the magnetic Curie point, and fundamentally and RE<sub>2</sub> Co<sub>14</sub>B is formed, this compound has a small crystal-anisotropy field, and since the coercive force as the whole magnet declines as the amount of alternatives of Co increases, it is good to stop [ of Fe ] to 20% or less more preferably 50% or less. Moreover, since there is an inclination for a residual magnetic flux density to fall when the amount of alternatives of nickel increases, to hold down to about 8% or less of Fe is desired.

[0018] Although the fundamental configuration element of a RE-TM-B system hot-working rare earth magnet is as above-mentioned, by making one or more sorts, such as Ag, Au, aluminum, Cu, Ga, Sn, Pt, and Zn, contain as an element of further others as occasion demands, coercive force can be heightened further and the effectiveness is effectively demonstrated by the addition more than 0.2 %. However, since a nonmagnetic grain boundary phase will increase and the fall of magnetic properties will be caused if many [ too ], it should stop to 2% or less.

[0019] Especially Ag, Au, aluminum, Cu, Pt, Sn, and Zn make the crystalline structure detailed also in the above-mentioned element, there is an operation which controls generation of the surface degradation layer accompanying hot working for anisotropy grant which mentions later, for example, the effectiveness of giving a magnet with the magnetic properties which were excellent even if it was the thing of the light-gage configuration which is about 3mm is demonstrated.

[0020] If hot working of the RE-TM-B system alloy obtained in this way is carried out and it carries out orientation at the temperature of 800 degrees C or more preferably, the permanent magnet of an anisotropy will be obtained. In addition, especially since this RE-TM-B system hot-working rare earth magnet has the effectiveness which was superior to the above-mentioned Re-B-Fe system sintering rare earth magnet in corrosion resistance or magnetic properties, it is desirable.

[0021] In this invention, the permanent magnet of high corrosion resistance can be obtained by performing each above-mentioned processing to the above RE-B-Fe system sintering rare earth magnets or a RE-TM-B system hot-working rare earth magnet. That is, the above-mentioned magnet alloy has very few amounts of the oxygen contained in it, or a rare-earth-elements oxide, and since the multiple oxide excellent in corrosion resistance is formed firmly, a surface protective effect is demonstrated that there is nothing with regret. Consequently, the rare earth magnet of this invention shows the corrosion resistance which stood high, continues at a long period of time, and can maintain the magnetic properties of a high level.

[0022]

[Example]

After having used Nd of iron powder of 99.9% of example 1 purity, the ferrobore alloy of 99.9% of purity, and 99.7% or more of purity as the raw material, blending these and carrying out the RF dissolution, it cast using water-cooled copper mold, and the presentation obtained the ingot of Nd<sub>14</sub>B<sub>7</sub> Fe<sub>79</sub>. After carrying out coarse grinding of this ingot with a stamp mill, it pulverized with the ball mill, and the impalpable powder whose particle size is 2.8-8 micrometers was obtained. While inserting this impalpable powder in metal mold and carrying out orientation in the field of 10KOe, they are 1.5 t/cm<sup>2</sup>. It fabricated by the pressure.

[0023] After sintering this Plastic solid at 1000 degrees C among Ar ambient atmosphere for 1 hour, it was cooled radiationally, and the rare earth magnet was obtained by carrying out aging treatment at 600 degrees C among Ar ambient atmosphere after that for 2

hours. The test piece of 20mmx30mmx3mm size was cut down from the obtained magnet, and the oxide film layer was formed after surface polish (No.150) and acetone cleaning on the conditions shown in Table 1. Moreover, based on a conventional method, a Watts bath is used and it is current density 8 A/dm<sup>2</sup>. What performed nickel plating was shown as an example of a comparison.

[0024] Magnetization processing was performed after the above-mentioned processing, respectively, and the test specimen which has the following initial magnetic properties was obtained.

Residual magnetic flux density (Br) = 12.5KG coercive force (iHc) = the corrosion resistance test was performed by the following approach about each test specimen obtained 12.0KQe energy product (BH) max = 35.0MGOe.

(Corrosion resistance test) a test specimen -- the constant temperature of 125 degree-Cx85%RH -- after leaving it in a constant humidity ambient atmosphere for 50 hours, an appearance (visual observation), adhesion (JIS K 5400: the squares tape method), and magnetic properties were investigated. The result is collectively shown in Table 1.

[0025]

[Table 1]

No.		表面処理	耐食性 試験後の 外観	耐食性 試験後の 密着性	試験後の磁気特性		
					Br (KG)	iHc (KOe)	(BH)max (MGOe)
実施例	1	200℃×1時間	○	○	12.5	12.0	35.0
	2	350℃×1時間	○	○	12.5	12.0	35.0
	3	445℃×0.2時間	○	○	12.5	12.0	35.0
	4	100 A/dm <sup>2</sup> ×2分	○	○	12.5	12.0	35.0
	5	250 A/dm <sup>2</sup> ×2分	○	○	12.5	12.0	35.0
	6	400 A/dm <sup>2</sup> ×1.5分	○	○	12.5	12.0	35.0
比較例	7	Ni (5.5μm)	×	×	12.0	11.8	29.0
	8	Ni (11 μm)	○	○	12.2	12.0	31.0

No. 1 ~ 3 : 大気雰囲気下

No. 4 : NaOH 50g/ℓ, 30°C

No. 5, 6 : NaOH 40g/ℓ, Na<sub>2</sub>SiO<sub>3</sub> 40g/ℓ, 30°C

外観評価基準 ○ : 変化無し、× : 赤錆発生

密着性評価基準 ○ : 剥離なし、× : 剥離あり

[0026] In the example (No.1-6), the appearance change after a corrosion resistance test and the fall of adhesion are not seen at all, but to maintaining the value before also examining magnetic properties as it is, appearance degradation by rusting and the fall of adhesion (plating adhesion) are remarkable, and magnetic properties are also falling considerably by the example of a comparison (7 No. 8) so that clearly also from Table 1.

[0027] The ferroboron of electrolytic iron of 99.9% of example 2 purity and 99.9% of purity and Pr of 99% or more of purity were used as the raw material, and after blending these, the ingot of the presentation shown in Table 2 using the water-cooled copper mold after the RF dissolution was obtained. After having cut this ingot, enclosing with the iron capsule and performing hot rolling of 76% of rates of the bottom of total pressure at 950 degrees C, the rare earth magnet of the magnetic properties shown in Table 2 was obtained by heat-treating on the conditions of 1000 degree-Cx 6 hours and, and 480 degree-Cx 2 hours. From this magnet, the 20mmx30mmx3mm test piece was cut down, oxidation treatment shown in Table 3 like an example 1 was performed after surface polish (No.150) and acetone cleaning, and magnetization processing and a corrosion resistance test were performed like the example 1 below. The result is shown in Table 3.

[0028]

[Table 2]

試料No.	組成 (原子%)	磁気特性		
		Br (KG)	iHc (KOe)	(BH) max (MGOe)
A	Pr9%-Nd6%-Fe79%-B5%-Ag1%	13.2	16	41
B	Pr15%-Fe73%-Co5%-B5%-Au2%	12.7	16	38
C	Pr8%-Nd7%-Fe78%-B5%-Pt2%	12.7	19	37
D	Pr8%-Nd7%-Fe79.5%-B5%-Sn0.5%	13.4	16	43

[0029]

[Table 3]

磁石 No.	酸化処理	耐食性 試験後の 外観	耐食性 試験後の 密着性	試験後の磁気特性		
				Br (KG)	iHc (KOe)	(BH) max (MGOe)
A	200 °C × 1 時間	○	○	13.2	16	41
	100 A / dm <sup>2</sup> × 1.5 分	○	○	13.2	16	41
B	412 °C × 0.1 時間	○	○	12.7	16	38
	100 A / dm <sup>2</sup> × 1.5 分	○	○	12.7	16	38
C	350 °C × 1 時間	○	○	12.7	19	37
	400 A / dm <sup>2</sup> × 0.8 分	○	○	12.7	19	37
D	220 °C × 0.8 時間	○	○	13.4	16	43
	480 °C × 0.1 時間	○	○	13.4	16	43
	320 A / dm <sup>2</sup> × 2.0 分	○	○	13.4	16	43

[0030] No test specimens shown in Tables 2 and 3 satisfy the requirements for a convention of this invention, and the fall of magnetic properties is not accepted in appearance degradation after a corrosion resistance test, and the fall list of adhesion at all.

[0031]

[Effect of the Invention] This invention is constituted as mentioned above, to a RE-B-Fe system sintering rare earth magnet or a RE-TM-B system hot-working rare earth magnet, by performing each above-mentioned processing, corrosion resistance can be raised remarkably and the RE-B-Fe system sintering rare earth magnet of high corrosion resistance or RE-TM-B system hot-working rare earth magnet which maintains outstanding magnetic properties for a long period of time can be offered.

[Translation done.]

# MANUFACTURE OF HIGHLY CORROSION-RESISTANT RARE-EARTH MAGNET

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## Abstract of JP5226129

PURPOSE: To provide a method for manufacturing a highly corrosion-resistant rare-earth magnet which can maintain improved magnetic characteristics over a long period of time without generating hydrogen occlusion, etc. CONSTITUTION: RE-B-Fe sintered rare-earth magnet or RE-TM-B hot machining rare-earth magnet is heated at 200-500 deg.C under oxidation atmosphere (a) or is anodized within an alkali liquid solution.

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(54)【発明の名称】 高耐食性希土類磁石の製造方法

(57)【要約】

【目的】 水素吸蔵等の問題を生じることなく、優れた磁気特性を長期間に亘って維持し得る様な高耐食性希土類磁石を製造する為の方法を提供する。

【構成】 R E - B - F e 系焼結希土類磁石または R E - T M - B 系熱間加工希土類磁石を、(a)酸化性雰囲気下にて200~500℃で加熱するか、または(b)アルカリ溶液中にて陽極酸化する。



## 【特許請求の範囲】

【請求項1】 RE-B-Fe系焼結希土類磁石またはRE-TM-B系熱間加工希土類磁石（REは希土類元素の1種以上、TMは遷移元素の1種以上をそれぞれ表わす）を、酸化性雰囲気下にて200～500℃で加熱することを特徴とする高耐食性希土類磁石の製造方法。

【請求項2】 RE-B-Fe系焼結希土類磁石またはRE-TM-B系熱間加工希土類磁石（REは希土類元素の1種以上、TMは遷移元素の1種以上をそれぞれ表わす）を、アルカリ性溶液中にて陽極電解することを特徴とする高耐食性希土類磁石の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、耐食性を高めて優れた磁気特性を長期間維持できる様にした高耐食性希土類磁石の製造する方法に関するものである。

## 【0002】

【従来の技術】磁石合金は、大型コンピュータの周辺機器から一般家庭用の各種電気製品等の電気もしくは電子部品用材料として幅広く利用されているが、特に近年におけるコンピュータや電気製品の小型化、高性能化の要求に伴って、磁石合金に対する磁気特性や耐食性等の要求性能はますます高度のものになっている。

【0003】こうした中においてRE-B-Fe系焼結希土類磁石及びRE-TM-B系熱間加工希土類磁石（REは希土類元素の1種以上、TMは遷移元素の1種以上をそれぞれ表わす：以下同じ）は磁気特性に優れたものであると期待されている。ところがこの希土類磁石は、非常に活性の高い希土類元素を含有するばかりでなく、REリッチ相とFeリッチ相が混在する合金であるため、両相間の電位差による局部電池の影響も加わって非常にさびやすいという欠点がある。従って実用化に当たっては防錆のための表面処理が不可欠であり、たとえばNiやZnなどの金属やそれらの合金をめっきする方法；りん酸塩処理やクロメート処理等の化成処理を施す方法；浸漬法やスプレー法等によりエポキシ系樹脂やアクリル系樹脂等の樹脂コーティングを施す方法等が提案されている。これらの中でもとくに汎用されているのは、複雑な設備を要することなく比較的安価に実施することのできるNiめっきあるいはNi-P等のNi合金めっき法である。

## 【0004】

【発明が解決しようとする課題】しかしながらNi等の金属もしくは合金をめっきする方法では、必ずしも満足いくめっき密着性および耐食性は得られない。その理由の1つは次の様に考えることができる。即ち、これらの希土類磁石は水素吸蔵性が高く、水素吸蔵によって脆化する性質があるので、NiまたはNi合金めっき法を採用すると、希土類磁石中にめっき時に発生する水素が吸蔵されてめっき界面で脆化割れを起こし、めっき剥離

を起こして耐食性を維持できなくなるものと考えられる。

【0005】こうした問題を回避するため、蒸着めっき等の気相めっき法も提案されているが、この方法ではめっき層のピンホール欠陥が耐食性向上の大きな障害となる。また浸漬法やスプレー法等によって樹脂コーティングを施す方法でも、十分な密着性と耐食性は得られ難く、しかも磁石表面に均一な樹脂コーティング被膜を形成することは困難であって、特に磁石のエッジ部は耐食性不足となり易く、この部分を起点として腐食が進行する。本発明は上記の様な状況に着目してなされたものであって、その目的は、水素吸蔵等の問題を生じることなく、優れた磁気特性を長期間に亘って維持し得る様な高耐食性希土類磁石を製造する為の方法を提供しようとするものである。

## 【0006】

【課題を解決するための手段】上記課題を解決することのできた本発明の構成は、RE-B-Fe系焼結希土類磁石またはRE-TM-B系熱間加工希土類磁石を、  
（a）酸化性雰囲気下にて200～500℃で加熱するか、または（b）アルカリ溶液中にて陽極酸化する点に要旨を有するものである。

## 【0007】

【作用】本発明によって希土類磁石の耐食性が向上する理由については全てを説明した訳ではないが、おそらくは、RE-B-Fe系焼結希土類磁石またはRE-TM-B系熱間加工希土類磁の表面に、通常の大気雰囲気下では形成されない様な、REおよびFe若しくはREおよびTMの酸化物、水酸化物および水和物等の混在した複合酸化物が強固に形成された為であると考えられる。尚この酸化物の組成はそれぞれの合金組成や酸化皮膜形成時の条件によって成分比が異なってくるものであり、一定になるものではないが、希土類磁石表面が酸化されたものであるため剥離の問題は生じない。更に上記複合酸化物は、水に対する溶解度が非常に低く、高温に対する安定性にも優れているので、永年の使用における磁気特性の劣化を抑制することができると考えられる。

【0008】酸化性雰囲気下で加熱する際の酸化性雰囲気は、大気下、酸素分圧調整下、水蒸気下等の様に、酸化を促進する環境下であればよく、特に限定されるものではない。但し処理温度は、200～500℃とするのが良く、200℃未満であれば上記複合酸化物を強固に形成することができず、500℃以上であれば磁石表面の酸化のみならず、粒界に析出しているREリッチ層の酸化が進行するので、割れが発生する恐れがある。

【0009】陽極酸化する際のアルカリ溶液としては、KOH、NaOH等のアルカリ金属水酸化物や、Na<sub>2</sub>SiO<sub>3</sub>、KAlO<sub>2</sub>等のアルカリ金属酸素酸塩等の1種または2種以上の水溶液であれば良く、この水溶液に可溶性塩を添加することもできる。また該水溶液のpH

は、アルカリ性であれば良いが、本発明に係る磁石の溶解が殆ど起こらない程の高アルカリ性であることが好ましく、具体的にはpH10以上であるのが良い。更に溶液温度、電流密度および溶解時間等の陽極電解条件は、溶液組成や合金組成に応じて適宜決定すれば良いが、特に電流密度は450A/dm<sup>2</sup>未満であることが好ましく、これ以上では形成された複合酸化物の破壊が促進されると考えられる。尚上記各処理を施した後、更にクロメート処理等の化成処理や酸化処理、有機コーティング層等を設けることによって耐食性を更に高めることも勿論可能である。

【0010】次に本発明で使用するRE-B-Fe系焼結希土類磁石およびRE-TM-B系熱間加工希土類磁石について説明する。まずRE-B-Fe系焼結希土類磁石は、希土類元素の少なくとも1種とBおよびFeを必須元素として含むものであり、REで示される希土類元素としては、Pr, Nd, La, Ce, Tb, Dy, Ho, Er, Eu, Sm, Gd, Pm, Tm, Yb, Lu, Yなどを挙げることができ、これらは単独で使用してもよく、或は必要により2種以上を併用することもできる。上記希土類元素の中でも特に好ましいのはPrとNdである。

【0011】これらRE-B-Fe系焼結希土類磁石中に占めるREの好ましい含有量（以下、特記しない限り原子%を意味する）は8~30%であり、8%未満では十分な保磁力が得られにくく、30%を超えると残留磁束密度が不足気味となる。またBの好ましい含有率は2~28%であり、2%未満では十分な保磁力が得られ難く、一方28%を超えると残留磁束密度が不十分となる。Feは40~90%の範囲が好ましく、40%未満では残留磁束密度が不足気味となり、一方90%を超えると高レベルの保磁力が得られ難くなる。

【0012】尚上記RE-B-Fe系焼結希土類磁石においては、Feの一部をCoやNiで置換することもできる。しかしCoの置換量が多くなり過ぎると高保磁力が得られにくくなるので、Feに対する置換量は50%以下に抑えるべきであり、またNi置換量が多くなり過ぎると残留磁束密度が低下する傾向があるので、Feに対する置換量は8%以下とすべきである。更にこの磁石には、他の元素として以下に示す様な元素の1種以上をFeに置換して含有させることによって保磁力を更に高めることが可能である。但し、2種以上を併用する場合の許容含有量は、各添加元素のうち最大値を示すものの含有量を上限とする。

【0013】Al: 9.5%以下、Ti: 4.5%以下、V: 9.5%以下、Cr: 8.5%以下、Mn: 8.0%以下、Bi: 5.0%以下、Nb: 9.5%以下、Ta: 9.5%以下、Mo: 9.5%以下、W: 9.5%以下、Sb: 2.5%以下、Ge: 7.0%以下、Sn: 3.5%以下、Zr: 5.

5%以下、Ni: 9.0%以下、Si: 9.0%以下、Zn: 1.1%以下、Hf: 5.5%以下。

【0014】次にRE-TM-B系熱間加工希土類磁石は、Yを含む希土類元素（RE）の少なくとも1種と遷移元素（TM）およびBを必須元素として含むものであり、REとしては前記RE-B-Fe系焼結希土類磁石の構成元素として挙げたものが再び例示されるが、これらのうち最も高い磁氣的性質はPrを用いたときに、得られ易いので、実質的にはPrのみ、もしくはREのうち50%以上がPrであるものが好ましい。またDyやTb等の重希土類元素を少量併用することは、保磁力の向上に有効である。

【0015】該RE-TM-B系熱間加工希土類磁石全量中に占めるREの好ましい含有量は、8~25%、より好ましくは10~20%、更に好ましくは12~18%の範囲である。REとTMおよびBを基本成分とする磁石の主相はRE<sub>2</sub>TM<sub>14</sub>B（たとえばPr<sub>2</sub>Fe<sub>14</sub>B）であるが、REが不足するとこの化合物が形成されず、α鉄と同一構造の立方晶組織となるため良好な磁氣的特性（特に保磁率）が得られ難く、他方、REが多過ぎると非磁性のREリッチ相が多くなって残留磁束密度が低下傾向を示す様になる。

【0016】次にBの含有量は、2~8%、より好ましくは4~6%が適当である。B量が不足する場合は、RE-Fe系の菱面体となるため満足な保磁力が得られ難く、逆に多過ぎるとたとえば非磁性のRE<sub>2</sub>Fe<sub>4</sub>B相が析出して残留磁束密度が低くなる。

【0017】TMは40~90%、より好ましくは65~90%が適当であり、TM量が不足すると残留磁束密度が低くなり、また多過ぎると保磁力が不十分となる。尚TMのうち最も代表的なものはFeであるが、その一部をCoおよび/またはNiで代替することができる。Coは磁石のキュリー点を上げるのに有効であり、基本的には主相のFeサイトを置換してRE<sub>2</sub>Co<sub>14</sub>Bを形成するが、この化合物は結晶異方性磁界が小さく、Coの代替量が多くなるにつれて磁石全体としての保磁力が低下するので、Feの50%以下、より好ましくは20%以下に抑えるのがよい。またNiの代替量が多くなると残留磁束密度が低下する傾向があるので、Feの8%程度以下に抑えることが望まれる。

【0018】RE-TM-B系熱間加工希土類磁石の基本的構成元素は上記の通りであるが、必要により更に他の元素としてAg, Au, Al, Cu, Ga, Sn, Pt, Zn等の1種以上を含有させることにより保磁力を更に高めることができ、その効果は0.2%以上の添加で有効に発揮される。しかし多過ぎると非磁性の粒界相が増加して磁氣特性の低下を招くので2%以下に抑えるべきである。

【0019】上記元素の中でも特にAg, Au, Al, Cu, Pt, Sn, Znは結晶組織を微細化し、後述す

るような異方性付与のための熱間加工に伴う表面劣化層の生成を抑制する作用があり、例えば 3mm 程度の薄肉形状のものであっても優れた磁気特性を持った磁石を与えるという効果を発揮する。

【0020】かくして得られる RE-TM-B 系合金を、好ましくは 800℃ 以上の温度で熱間加工して配向させると、異方性の永久磁石が得られる。尚この RE-TM-B 系熱間加工希土類磁石は、耐食性や磁気特性において前述の Re-B-Fe 系焼結希土類磁石よりも優れた効果を有しているので特に好ましい。

【0021】本発明では、上記のような RE-B-Fe 系焼結希土類磁石もしくは RE-TM-B 系熱間加工希土類磁石に対し、上記各処理を施すことによって、高耐食性の永久磁石を得ることができる。即ち上記の磁石合金は、その中に含まれる酸素や希土類元素酸化物の量が非常に少なく、且つ耐食性に優れた複合酸化物が強固に形成されるので、表面保護効果が遺憾なく発揮される。その結果、本発明の希土類磁石は卓越した耐食性を示し、高レベルの磁気特性を長期間に亘って維持し得るものとなる。

【0022】

【実施例】

実施例 1

純度 99.9% の鉄粉、純度 99.9% のフェロボロン合金および純度 99.7% 以上の Nd を原料とし、これらを配合して高周波溶解した後水冷銅鑄型を用いて鑄造し、組成が Nd<sub>14</sub>B<sub>7</sub>Fe<sub>79</sub> の鑄塊を得た。この鑄塊をスタ

ンプミルで粗粉碎した後ボールミルで微粉碎し、粒径が 2.8~8 μm の微粉末を得た。この微粉末を金型に装入して、10 KOe の磁界中で配向させると共に 1.5 t/cm<sup>2</sup> の圧力で成形した。

【0023】この成形体を、Ar 雰囲気中 1000℃ で 1 時間焼結した後放冷し、その後 Ar 雰囲気中 600℃ で 2 時間時効処理することにより希土類磁石を得た。得られた磁石より 20mm×30mm×3mm サイズの試験片を切り出し、表面研磨 (No. 150) およびアセトン脱脂後、表 1 に示す条件で酸化皮膜層を形成した。また従来法に準拠し、ワット浴を用いて電流密度 8 A/dm<sup>2</sup> で Ni めっきを行なったものを比較例として示した。

【0024】上記処理の後夫々着磁処理を行ない、下記の初期磁気特性を有する供試材を得た。

残留磁束密度 (B<sub>r</sub>) = 12.5 KG

保磁力 (iH<sub>c</sub>) = 12.0 KQe

エネルギー積 (BH)<sub>max</sub> = 35.0 MGOe

得られた各供試材について下記の方法で耐食性試験を行なった。

(耐食性試験) 供試材を 125℃×85%RH の恒温恒湿雰囲気中に 50 時間放置した後、外観 (目視観察)、密着性 (JIS K 5400: 基盤目テープ法) および磁気特性を調べた。その結果を表 1 に一括して示す。

【0025】

【表 1】



No.		表面処理	耐食性試験後の外観	耐食性試験後の密着性	試験後の磁気特性		
					Br (KG)	iHc (KOe)	(BH)max (MGOe)
実施例	1	200℃×1時間	○	○	12.5	12.0	35.0
	2	350℃×1時間	○	○	12.5	12.0	35.0
	3	445℃×0.2時間	○	○	12.5	12.0	35.0
	4	100 A/dm <sup>2</sup> × 2分	○	○	12.5	12.0	35.0
	5	250 A/dm <sup>2</sup> × 2分	○	○	12.5	12.0	35.0
	6	400 A/dm <sup>2</sup> × 1.5分	○	○	12.5	12.0	35.0
比較例	7	Ni (5.5μm)	×	×	12.0	11.8	29.0
	8	Ni (11 μm)	○	○	12.2	12.0	31.0

No. 1～3 : 大気雰囲気下  
No. 4 : NaOH 50g/ℓ, 30℃  
No. 5, 6 : NaOH 40g/ℓ, Na<sub>2</sub>SiO<sub>3</sub> 40g/ℓ, 30℃  
外観評価基準 ○: 変化無し、×: 赤錆発生  
密着性評価基準 ○: 剥離なし、×: 剥離あり

【0026】表1からも明らかであるように、実施例（No. 1～6）では耐食性試験後の外観変化および密着性の低下は全く見られず、磁気特性も試験前の値をそのまま維持しているのに対し、比較例（No. 7, 8）では発錆による外観劣化および密着性（めっき密着性）の低下が著しく、また磁気特性もかなり低下している。

【0027】実施例2  
純度99.9%の電解鉄と純度99.9%のフェロボロンおよび純度99%以上のPrを原料とし、これらを配合した後高周波溶解後水冷銅鑄型を用いて表2に示す組成の鑄塊を得た。この鑄塊を切断して鉄製カプセルに封

入し、950℃にて全圧下率76%の熱間圧延を行なった後、1000℃×6時間および480℃×2時間の条件で熱処理することにより、表2に示す磁気特性の希土類磁石を得た。この磁石より20mm×30mm×3mmの試験片を切り出し、表面研磨（No. 150）およびアセトン脱脂の後、実施例1と同様にして表3に示す酸化処理を施し、以下実施例1と同様にして着磁処理および耐食性試験を行なった。その結果を表3に示す。

【0028】  
【表2】

試料No.	組成 (原子%)	磁気特性		
		Br (KG)	iHc (KOe)	(BH)max (MGOe)
A	Pr9%-Nd6%-Fe79%-B5%-Ag1%	13.2	16	41
B	Pr15%-Fe73%-Co5%-B5%-Au2%	12.7	16	38
C	Pr8%-Nd7%-Fe78%-B5%-Pt2%	12.7	19	37
D	Pr8%-Nd7%-Fe79.5%-B5%-Sn0.5%	13.4	16	43

【0029】  
【表3】



磁 石 No.	酸 化 処 理	耐食性 試験後の 外 観	耐食性 試験後の 密着性	試験後の磁気特性		
				Br (KG)	iHc (KOe)	(BH)max (MGOe)
A	200 °C × 1 時間	○	○	13.2	16	41
	100 A / dm <sup>2</sup> × 1.5 分	○	○	13.2	16	41
B	412 °C × 0.1 時間	○	○	12.7	16	38
	100 A / dm <sup>2</sup> × 1.5 分	○	○	12.7	16	38
C	350 °C × 1 時間	○	○	12.7	19	37
	400 A / dm <sup>2</sup> × 0.8 分	○	○	12.7	19	37
D	220 °C × 0.8 時間	○	○	13.4	16	43
	480 °C × 0.1 時間	○	○	13.4	16	43
	320 A / dm <sup>2</sup> × 2.0 分	○	○	13.4	16	43

【0030】表2、3に示した供試材は、いずれも本発明の規定要件を満たすものであり、耐食性試験後の外観劣化および密着性の低下並びに磁気特性の低下は全く認められない。

【0031】

【発明の効果】本発明は以上の様に構成されており、R

E-B-F e系焼結希土類磁石またはRE-TM-B系熱間加工希土類磁石に対して、上記各処理を施すことによって耐食性を著しく高めることができ、優れた磁気特性を長期間維持する高耐食性のRE-B-F e系焼結希土類磁石またはRE-TM-B系熱間加工希土類磁石を提供し得ることになった。